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(54) Title: POLYMER NANOCOMPOSITE COMPOSITION			
(57) Abstract A polymer nanocomposite composition of a polyamide and a treated silicate, wherein the treated silicate includes a silicate material treated with at least one ammonium ion of the formula: $^+NR_1R_2R_3R_4$ wherein R_1 , R_2 , R_3 and R_4 are independently selected from a group consisting of a saturated or unsaturated C_1 to C_{22} hydrocarbon, substituted hydrocarbon and branched hydrocarbon, or where R_1 and R_2 form a N,N-cyclic ether, and optionally, one of R_1 , R_2 , R_3 and R_4 is hydrogen.			

POLYMER NANOCOMPOSITE COMPOSITION

Field of the Invention

5 This invention relates to a nanocomposite material comprising a polyamide matrix having dispersed therein a treated silicate. More particularly, this invention relates to a nanocomposite material having dispersed therein a silicate
10 material treated with at least one ammonium ion.

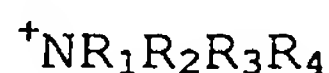
Background of the Invention

International Application WO 93/04118 discloses a process of preparing a polymer nanocomposite having platelet particles dispersed therein. The process involves melt-processing the
15 polymer with a swellable and polymer-compatible intercalated layered material and subjecting it to a shear rate sufficient to dissociate the layers. The layered material is compatibilized with one or more "effective swelling/compatibilizing agents" having a silane function or an onium cation function.

20 International Application WO 93/04117 discloses a process of preparing a polymer nanocomposite having platelet particles dispersed therein, where the polymer and the swellable and polymer-compatible intercalated layered material are melt-processed. The layered material is compatibilized with one or
25 more "effective swelling/compatibilizing agents" selected from primary ammonium, secondary ammonium and quaternary phosphonium ions. The selected swelling/compatibilizing agents "...render their surfaces more organophilic than those compatibilized by tertiary and quaternary ammonium ion complexes...", facilitate
30 exfoliation, resulting in less shear in mixing and less decomposition of the polymer, and heat stabilize the composite more than other cations (such as quaternary ammonium cation) swelling/compatibilizing agents.

stability. The composition processes well and tolerates a wide range of molding conditions.

Such polymer nanocomposite composition comprises a polyamide and a treated silicate, wherein the treated silicate includes a silicate material treated with at least one ammonium ion of the formula:



wherein:

R_1 , R_2 , R_3 and R_4 are independently selected from a group consisting of a saturated or unsaturated C_1 to C_{22} hydrocarbon, substituted hydrocarbon and branched hydrocarbon, or where R_1 and R_2 form a N,N-cyclic ether. Examples include saturated or unsaturated alkyls, including alkylenes; substituted alkyls such as hydroxyalkyls, alkoxyalkyls, alkoxys, amino alkyls, acid alkyls, halogenated alkyls, sulfonated alkyls, nitrated alkyls and the like; branched alkyls; aryls and substituted aryls, such as alkylaryls, alkyoxyaryls, alkylhydroxyaryls, alkylalkoxyaryls and the like. Optionally, one of R_1 , R_2 , R_3 and R_4 is hydrogen. The milligrams of treatment per 100 grams of silicate (MER) of the treated silicate, described in more detail below, is from about 10 milliequivalents/100 g below the cation exchange capacity of the untreated silicate to about 30 milliequivalents/100 g above the cation exchange capacity of the untreated silicate. The composite polymer matrix material demonstrates, when tested, an improvement in tensile modulus and flexural modulus, without a substantial decrease in tensile strength, when compared to that of the polymer without the treated silicate. As utilized herein, "substantial decrease" means a decrease exceeding the statistically determined deviations.

The present invention further relates to a process to prepare the above polymer nanocomposite composition comprising forming a flowable mixture of a polyamide and a treated silicate

art as nylons, which can be obtained from diamines and dibasic acids having the recurring unit represented by the general formula:



- 5 in which R_5 is an alkylene group of at least 2 carbon atoms, preferably from about 2 to about 11 or arylene having at least about 6 carbon atoms, preferably about 6 to about 17 carbon atoms; and R_6 is selected from R_5 and aryl groups. Also, included are copolyamides, terpolyamides and the like obtained by
10 known methods, for example, by condensation of hexamethylene diamine and a mixture of dibasic acids consisting of terephthalic acid and adipic acid. Polyamides of the above description are well-known in the art and include, for example,
15 poly(hexamethylene adipamide) (nylon 6,6), poly(hexamethylene sebacamide) (nylon 6,10), poly(hexamethylene isophthalamide), poly(hexamethylene terephthalamide), poly(heptamethylene pimelamide) (nylon 7,7), poly(octamethylene suberamide) (nylon 8,8), poly(nonamethylene azelamide) (nylon 9,9), poly
20 (decamethylene sebacamide) (nylon 10,9), poly(decamethylene sebacamide) (nylon 10,10), poly[bis(4-amino cyclohexyl)methane-1,10-decanecarboxamide)], poly(m-xylene adipamide), poly(p-xylene sebacamide), poly(2,2,2-trimethyl hexamethylene terephthalamide), poly(piperazine sebacamide), poly(p-phenylene terephthalamide), poly(metaphenylene isophthalamide), and copolymers and
25 terpolymers of the above polymers. Additional polyamides include nylon 4,6, nylon 6,9, nylon 6,10, nylon 6,12, nylon 11, nylon 12, amorphous nylons, aromatic nylons and their copolymers.

Other useful polyamides are those formed by polymerization of amino acids and derivatives thereof, as for example, lactams.

- 30 Illustrative of these useful polyamides are poly(caprolactam) (nylon 6), poly(4-aminobutyric acid) (nylon 4), poly(7-aminoheptanoic acid) (nylon 7), poly(8-aminooctanoic acid) (nylon 8), poly(9-aminononanoic acid) (nylon 9), poly(10-aminodecanoic

Among the preferred embodiments is nylon 6, nylon 6,6, blends thereof and copolymers thereof. The range of ratios of the nylon 6/nylon 6,6 in the blends is from about 1/100 to 100/1.

Preferably, the range is from about 1/10 to 10/1. The range of ratios of the nylon 6/nylon 6,6 in the copolymers is about 1/100 to 100/1. Preferably, the range is from about 1/10 to 10/1.

Optionally, the nanocomposite composition comprises at least one additional polymer. Examples of suitable polymers include polyethyleneoxide, polycarbonate, polyethylene, polypropylene, poly(styrene-acrylonitrile), poly(acrylonitrile-butadiene-styrene), poly(ethylene terephthalate), poly(butylene terephthalate), poly(trimethylene terephthalate), poly(ethylene naphthalate), poly(ethylene terephthalate-co-cyclohexane dimethanol terephthalate), polysulphone, poly(phenylene oxide) or poly(phenylene ether), poly(hydroxybenzoic acid-co-ethylene terephthalate), poly(hydroxybenzoic acid-co-hydroxynaphthenic acid), poly(esteramide), poly(etherimide), poly(phenylene sulfide), poly(phenylene terephthalamide).

The mixture may include various optional components which are additives commonly employed with polymers. Such optional components include surfactants, nucleating agents, coupling agents, fillers, impact modifiers, chain extenders, plasticizers, compatibilizers, colorants, mold release lubricants, antistatic agents, pigments, fire retardants, and the like.

Suitable examples of fillers include carbon fiber, glass fiber, kaolin clay, wollastonite and talc. Suitable examples of compatibilizers include acid-modified hydrocarbon polymer, such as maleic anhydride-grafted propylene, maleic anhydride-grafted polypropylene, maleic anhydride-grafted ethylenebutylene-styrene block copolymer. Suitable examples of mold release lubricant includes alkyl amine, stearamide, and di- or tri-aluminum stearate.

polyamide is bonded to a surface of the treated layered silicate by a silane coupling agent.

The silicate materials of the present invention are selected from the group consisting of layered silicates and fibrous, chain-like silicates, and include phyllosilicates. Examples of fibrous, chain-like silicates include chain-like minerals, for example sepiolite and attapulgite, with sepiolite being preferred. Such silicates are described, for example, in Japanese Patent Application Kokoku 6-84435 published October 26, 1994. Examples of layered silicates include layered smectite clay minerals such as montmorillonite, nontronite, beidellite, volkonskoite, Laponite® synthetic hectorite, natural hectorite, saponite, sauconite, magadiite, and kenyaite; vermiculite; and the like. Other useful materials include layered illite minerals such as ledikite and admixtures of illites with one or more of the clay minerals named above. The preferred layered silicates are the smectite clay minerals such as montmorillonite, nontronite, beidellite, volkonskoite, Laponite® synthetic hectorite, natural hectorite, saponite, sauconite, magadite, and kenyaite.

The layered silicate materials suitable for use in the present invention are well-known in the art, and are sometimes referred to as "swellable layered material". A further description of the claimed layered silicates and the platelets formed when melt processed with the polyamide is found in International Patent Application WO 93/04117, which is hereby incorporated by reference. The layered silicate materials typically have planar layers arrayed in a coherent, coplanar structure, where the bonding within the layers is stronger than the bonding between the layers such that the materials exhibit increased interlayer spacing when treated.

The layered silicate materials require treatment as described in more detail below with the subject ammonium ion to

unsaturated tallow or a hydrocarbon having at least 6 carbons, and R₂, R₃ and R₄ independently have from one to eighteen carbons.

Tallow is composed predominantly of octadecyl chains with small amounts of lower homologues, with an average of from 1 to 2 degrees of unsaturation. The approximate composition is 70% C₁₈, 25% C₁₆, 4% C₁₄ and 1% C₁₂. In another preferred embodiment of the present invention, R₁ and R₂ are independently selected from the group consisting of hydrogenated tallow, unsaturated tallow or a hydrocarbon having at least 6 carbons and R₃ and R₄ independently have from one to twelve carbons.

Examples of suitable R₁, R₂, R₃ and R₄ groups are alkyl such as methyl, ethyl, octyl, nonyl, tert-butyl, ethylhexyl, neopentyl, isopropyl, sec-butyl, dodecyl and the like; alkenyl such as 1-propenyl, 1-butenyl, 1-pentenyl, 1-hexenyl, 1-heptenyl, 1-octenyl and the like; cycloalkyl such as cyclohexyl, cyclopentyl, cyclooctyl, cycloheptyl and the like; alkoxy such as ethoxy; hydroxyalkyl; alkoxyalkyl such as methoxymethyl, ethoxymethyl, butoxymethyl, propoxyethyl, pentoxybutyl and the like; aryloxyalkyl and aryloxyaryl such as phenoxyphenyl, phenoxymethyl, phenoxydecyl, phenoxyoctyl and the like; arylalkyl such as benzyl, phenylethyl, 8-phenyloctyl, 10-phenyldecyl and the like, alkylaryl such as 3-decylphenyl, 4-octylphenyl, nonylphenyl and the like.

The preferred ammoniums used in treating the silicate materials include oniums such as dimethyldi(hydrogenated tallow) ammonium, dimethylbenzyl hydrogenated tallow ammonium, dimethyl(ethylhexyl) hydrogenated tallow ammonium, trimethyl hydrogenated tallow ammonium, methylbenzyldi(hydrogenated tallow) ammonium, N,N-2-cyclobutoxydi(hydrogenated tallow) ammonium, trimethyl tallow ammonium, methyldihydroxyethyl tallow ammonium, octadecylmethyldihydroxyethyl ammonium, dimethyl(ethylhexyl) hydrogenated tallow ammonium and mixtures thereof. Particularly preferred ammoniums include quaternary ammoniums, for example,

nanocomposite sample may have a higher concentration of treated silicate but a lower concentration of silicate, than a second nanocomposite sample, because the first sample has a higher MER than the second sample.

5 If the MER value of the treated silicate is substantially less than its exchange capacity, for example about 85 MER for the preferred montmorillonite, there is too little of the cationic treatment to have a beneficial effect. If the MER exceeds about 125, the excess ammonium may be detrimental to the properties of
10 the nylon. Preferably, when the untreated montmorillonite has an exchange capacity of 95, the treated layered silicate has a cation exchange capacity of from about 85 to about 125.

 The amount of treated silicate included in the composition is in the range of about 0.1 to 12 weight % of the composite.
15 The concentration is adjusted to provide a composite polymer matrix material which demonstrates, when tested, an increase in tensile modulus and flexural modulus, without a decrease in tensile strength. Preferably, the increase in tensile modulus and flexural modulus is at least about 10%. More preferably, the
20 increase in tensile modulus and flexural modulus is at least about 20%. Too little treated silicate fails to provide the desired increase in tensile modulus and flexural modulus. Too much treated silicate provides a polyamide composite with a decreased tensile strength. Further, it may be desirable to have
25 the crystalline regions of the polyamide in the nanocomposite composition be less than 1.0 μ m.

 The particle size of the treated silicate is such that optimal contact between the polymer and the treated silicate is facilitated. The range of particle size can vary from about 10
30 microns to about 100 microns. Preferably, the particle size is in the range of from about 20 to 80 microns. Most preferably, the particle size is below about 30 microns, such as those that

Said cationic dyes would impart color-fastness and uniformity of color in addition to increasing the intercalation of the polymer molecules.

5 It is further desirable to have a polymer composite that provides both the desired strength and flexibility, and yet is lightweight. This is accomplished by minimizing the concentration of treated silicate in the nanocomposite. The preferred nanocomposite contains a concentration of treated silicate of from about 0.1 to about 12.0 weight % of the
10 composite. The most preferred nanocomposite contains a concentration of treated silicate of from about 0.5 to about 6.0 weight % of the composite.

In a first embodiment of the present invention, the nanocomposite composition is prepared using a two step process.
15 One step includes forming a flowable mixture of the polyamide as a polymer melt and the treated silicate material. The other step includes dissociating at least 50% but not all of the treated silicate material. The term "dissociating", as utilized herein, means delaminating or separating treated silicate material into
20 submicron-scale structures comprising individual or small multiple units. For the embodiment wherein layered silicates are utilized this dissociating step includes delaminating the treated silicate material into submicron scale platelets comprising individual or small multiple layers. For the embodiment wherein
25 fibrous, chain-like silicates are utilized, this dissociating step includes separating the treated silicate material into sub-micron scale fibrous structures comprising individual or small multiple units.

As referred to in the mixture forming step, a flowable
30 mixture is a mixture which is capable of dispersing dissociated treated silicate material at the submicron scale. A polymer melt is a melt processable polymer or mixture of polymers which has been heated to a temperature sufficiently high to produce a

ethylacrylate, ethylene-ethylmethacrylate or ethylene methacrylate. Examples include Iotek® ionomer and Escor® ATX acid terpolymer, both available from Exxon. The polyamide polymers suitable for the carrier polymer include nylons such as
5 nylon 6, nylon 6,6, nylon 4,6, nylon 6,9, nylon 6,10, nylon 6,12, nylon 11, nylon 12, amorphous nylons, aromatic nylons and their copolymers. The polymer of the carrier may be the same as or different from the polyamide of the flowable mixture. For example, both polymers may be a polyamide, particularly nylon
10 6,6, but may have the same or different molecular weight. The preferred weight average molecular weight of the carrier polymer of the concentrate is in the range of about 5,000 D to about 60,000 D. The most preferred range of the weight average molecular weight for the carrier polymer is in the range of about
15 10,000 to about 40,000 D. In this embodiment, the dissociation step of the present process, as described below, may occur at least in part via the forming of the concentrate such that the dissociation step may precede the step of forming the flowable mixture. It is therefore understood that the process steps
20 (e.g., forming and dissociating) may occur sequentially without regard to order, simultaneously or a combination thereof. In the second step, the flowable mixture is sufficiently mixed to form the dispersed nanocomposite structure of dissociated silicate in the polymer melt, and it is thereafter cooled. The
25 silicate can be dissociated by being subjected to a shear having an effective shear rate. As used herein, an effective shear rate is a shear rate which is effective to aid in dissociation of the silicate and provide a composition comprising a polyamide matrix having silicate substantially homogeneously dispersed therein
30 without substantially breaking the individual units (e.g., platelets or fibrous chains).

Any method which can be used to apply a shear to a flowable mixture or any polymer melt can be used. The shearing

Optionally, an additional processing step can be added, such as solid state polymerization, wherein the compounded pellets are held for several hours at a high temperature below the melting point of the polymer. For example, typical solid state polymerization conditions are heating the solid polymer in the range of about 200 to 240°C for a period of from about two (2) to five (5) hours. Said additional processing step results in an increase in molecular weight and an improvement in toughness, ductility and tensile strength of the nanocomposite.

Another optional processing step can be a heat treatment step, where the composition is heated to improve intercalation of the nylon molecules into the silicate structure. Said heat treatment step is performed by heating the composition at a temperature in the range of about 200 to 240°C for a period of about two (2) to five (5) hours.

Another preferred continuous compounder is the Farrel Continuous Mixer (FCM). For composites using Vydyne® 21 nylon, the preferred temperature of the melt is in the range from about 275 to 315°C, with the most preferred range being from about 275 to 295°C.

The polymer melt containing nano-dispersed dissociated silicate material may also be formed by reactive extrusion in which the silicate material is initially dispersed as aggregates or at the nanoscale in a liquid or solid monomer and this monomer is subsequently polymerized in an extruder or the like. Alternatively, the polymer may be granulated and dry mixed with the treated silicate material, and thereafter, the composition may be heated in a mixer until the polymer is melted forming the flowable mixture.

The process to form the nanocomposite is preferably carried out in the absence of air, as for example in the presence of an inert gas, such as argon, neon or nitrogen. The process

Examples

The following examples are presented to further illustrate the invention and do not limit the scope of the claims in any manner.

- 5 All of the nylons used in the following examples are nylon 6,6. Unless otherwise indicated, the nylon used was nylon h, manufactured by Solutia, Inc, and characterized in the Table of Nylon Types, below. Unless otherwise indicated, all percents are weight percent. The % clay is the total weight of pristine clay
10 in the final composite, be it pristine or pre-treated. Tensile strength and Young's Modulus are measured according to ASTM method D638 and are reported in kpsi and MPa. Flexural modulus is measured according to ASTM method D790 and is reported in kpsi and MPa.
- 15 The runs numbered with a "-C" are control runs.

AA dimethylbenzyl hydrogenated tallow 95

Table of Nylon Types

	<u>Nylon</u>	<u>Amine Ends</u>	<u>Acid Ends</u>	<u>Amine/Acid</u>	<u>M_w</u>
					(1000 D)
	a	55	60	0.92	35
5	b	35	60	0.58	42
	c	40	40	1.00	50
	d	15	50	0.30	62
	e	80	50	1.60	31
	f	125	70	1.79	21
10	g	31	60	0.52	44
	h	45	70	0.64	35

The amine ends and the acid ends are the equivalents of unreacted amine and acid functional groups on the nylon. The M_w is the weight average molecular weight as measured in Daltons.

Table 1.
Control Runs
(Clays not treated with Quaternary Amines)

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
1-C	--	0	11.6 (80.3)	412 (2860)	425 (2940)	286
2-C	A	3.6	11.2 (77.7)	449 (3110)	463 (3210)	285
3-C	A	6.5	11.6 (80.7)	466 (3230)	463 (3210)	286
4-C	B	7.1	11.3 (78.1)	481 (3330)	482 (3340)	286
5-C	--	0	11.6 (80.7)	445 (3080)	436 (3020)	280
6-C	C	2.9	9.65 (66.9)	494 (3420)	481 (3330)	291
7-C	C	8.8	8.08 (56.0)	576 (3990)	568 (3940)	293
8-C	D	4.8	9.11 (63.1)	580 (4020)	550 (3810)	285

Table 2
Control Runs
(Treated Clays with MER's Exceeding 125)

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
9-C	--	0	11.3 (78.3)	417 (2980)	432 (2990)	286
10-C	G	13.3	9.78 (67.8)	610 (4230)	613 (4250)	286
11-C	--	0	11.2 (77.4)	423 (2930)	416 (2880)	277
12-C	E	4.2	10.6 (73.4)	520 (3600)	455 (3150)	277
13-C	E	4.4	10.6 (73.2)	500 (3460)	471 (3260)	279
14-C	E	9.6	9.48 (65.7)	553 (3830)	501 (3470)	285
15-C	--	0	11.3 (78.4)	430 (2980)	445 (3080)	286
16-C	H	11.6	7.47 (51.8)	582 (4030)	573 (3970)	291
17-C	H	11.8	7.73 (53.6)	561 (3890)	549 (3760)	285
18-C	H	6.0	10.6 (73.1)	523 (3620)	516 (3580)	288
19-C	H	11.8	5.41 (37.5)	593 (4110)	571 (3960)	295
20-C	H	6.0	10.5 (72.6)	510 (3530)	507 (3510)	283
21-C	H	8.9	10.3 (71.1)	555 (3850)	541 (3750)	289
22-C	--	0	12.0 (82.9)	424 (2940)	432 (3850)	285
23-C	F	7.3	11.2	557	555	287

Table 3
Quaternary Ammonium Treated Clays

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
24-C	--	0	11.6 (80.7)	445 (3080)	436 (3020)	280
25	P	3.0	12.5 (86.3)	580 (4020)	539 (3740)	292
26	P	5.8	11.6 (80.7)	657 (4550)	633 (4390)	293
27	S	3.3	12.1 (84.0)	524 (3630)	524 (3630)	291
28	T	5.4	12.0 (83.2)	596 (4130)	558 (3870)	288
29-C	--	0	11.4 (78.7)	443 (3070)	425 (2940)	285
30	I	1.8	11.6 (80.4)	509 (3530)	470 (3260)	286
31	R	0.6	12.4 (85.9)	482 (3340)	457 (3170)	286
32	M	0.6	11.5 (79.8)	457 (3170)	438 (3040)	285
33	N	1.6	12.1 (83.9)	504 (3490)	474 (3280)	286
34-C	--	0	11.5 (79.5)	463 (3190)	429 (2960)	286
35	J	1.0	10.3 ¹ 453 (71.5)	448 (3140)	284 (3100)	
36	J	3.3	11.3 ² 500 (78.5)	496 (3460)	288 (3440)	
37	L	2.5	12.0 (83.4)	525 (3640)	502 (3480)	284
38	L	3.3	11.8 (81.6)	535 (3710)	516 (3580)	286
1 ±1.44		² ±0.98				

In Table 4, composites are prepared from eight (8) different quaternary ammonium-treated clay processed with a ZSK twin screw extruder are shown. All of the composites show an increase in tensile modulus and flexural modulus without a decrease in tensile strength when compared to samples without treated clay.

Table 4, Continued
Quaternary Ammonium Treated Clays

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
58-C	--	0	11.5 (80.0)	445 (3080)	431 (2990)	287
59	U	2.1	11.8 (82.1)	475 (3290)	483 (3350)	287
60	U	5.2	11.6 (80.1)	560 (4020)	540 (3740)	287
61	U ¹	5.3	12.1 (83.4)	575 (3970)	555 (3830)	287
62	U ²	5.3	12.3 (84.8)	564 (3890)	539 (3720)	288
63-C	--	0	11.31 (78.4)	430 (3880)	445 (3080)	286
64	X	4.9	11.76 (81.5)	606 (4200)	568 (3940)	288
65	X	6.4	11.27 (78.1)	573 (3970)	604 (4190)	295
66-C	--	0	11.55 (79.7)	423 (2930)	424 (2930)	286
67	Q	3.0	11.63 (80.6)	487 (3380)	456 (3160)	286
68	Q	6.5	11.61 (80.5)	514 (3560)	515 (3570)	288
69	Q	11.1	11.60 (80.4)	659 (4570)	579 (4010)	290
70	Q	11.4	12.47 (86.4)	782 (5420)	622 (4310)	289

¹ Second pass of example 60 through ZSK mixer.

² Third pass of example 60 through ZSK mixer.

In Table 5, the following four (4) nylon 6,6 products were used to prepare composites: nylon d, nylon c, nylon b, nylon h, shown in the Table of Nylon Types. The nylons are presented above in order of decreasing average molecular weight. The
5 composites were processed using a ZSK twin screw extruder.

All composites show an increase in tensile modulus and flexural modulus without a decrease in tensile strength when compared to samples without treated clay.

In Table 6, composites using polymer blends of nylon h and nylon b were made. One blend, example 85, was made by preparing a clay concentrate in nylon h, such as control sample 83-C, and then blending the concentrate with a second polymer, such as b.

- 5 The second blend, example 86, was made by preparing a clay concentrate of nylon b, and blending in the nylon h. The composites were processed using a ZSK twin screw extruder.

In Table 7, a concentrate of the treated clay and a polymer other than a polyamide is let down, or diluted with the nylon h. The controls are a mixture of the polymer neat and nylon h.

The runs in Table 8 vary the feed points for processing the nylon with the treated clay. The clay was fed into the ZSK twin screw extruder at the throat or downstream of the throat. The nylon used was a copolymer of 80% nylon 6,6 and 20% nylon 6.

In Table 9, composites are prepared from eight (8) different quaternary ammonium/ammonium blend-treated silicates. The composites are processed using a ZSK twin screw extruder. Taking into account the standard deviations of the tensile strength measurements, all of the samples show an increase in tensile modulus and flex modulus without a decrease in tensile strength. Samples 125 through 135 show the effect of varying the nylon type.

Table 9, Continued
Ammonium Blend-Treated Clays

Run #	Clay Type	Clay (%)	Tensile Strength kpsi (MPa)	Tensile Modulus kpsi (MPa)	Flex Modulus kpsi (MPa)	Melt Temp. (°C)
114-C	--	0	11.2 (77.2)	411 (2830)	405 (2790)	287
115	KK	2.8	11.5 (79.3)	470 (3240)	475 (3280)	287
116	KK	6.2	10.9 ¹ 494 (75.2)	536 (3410)	288 (3700)	
117	LL	3.4	11.6 (80.0)	500 (3450)	510 (3520)	288
118	LL	6.7	11.0 ² 544 (75.9)	542 (3750)	288 (3740)	
119	MM	3.2	11.5 (79.3)	480 (3310)	497 (3430)	287
120	MM	6.5	11.0 ³ 529 (75.9)	540 (3670)	288 (3720)	
121-C	--	0	11.6 (80.0)	427 (2940)	466 (3210)	282
122	NN	3.5	12.6 (86.9)	522 (3600)	568 (3920)	282
123	NN	6.5	12.6 (86.9)	572 (3940)	623 (4300)	282
124	NN	8.4	11.3 ⁴ 650 (77.9)	664 (4480)	283 (4580)	

¹ Standard Deviation of ± 1.22

² Standard Deviation of ± 0.24

³ Standard Deviation of ± 0.49

⁴ Standard Deviation of ± 0.60

In Table 10, composites are prepared from six (6) different tertiary ammonium-treated silicates. The composites are processed using a ZSK twin screw extruder. Taking into effect the standard deviation of the tensile strength
5 measurements, all of the samples show an increase in tensile modulus and flex modulus without a decrease in tensile strength.

In Table 11, samples 147, 150, 152, 154 and 156 are subjected to solid state polymerization. A dramatic improvement is noted in the tensile strength and elongation.

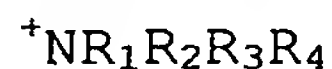
Claims:

1. A polymer nanocomposite composition comprising:

(1) a polyamide, and

5 (2) treated silicate, wherein

said silicate material comprises silicate material treated with
at least one ammonium ion of the formula:



wherein R_1 , R_2 , R_3 and R_4 are independently selected from a
10 group consisting of a saturated or unsaturated C_1 to C_{22}
hydrocarbon, substituted hydrocarbon and branched hydrocarbon, or
where R_1 and R_2 form a N,N-cyclic ether; wherein,
optionally, one of R_1 , R_2 , R_3 and R_4 is hydrogen;

wherein the MER of the treated silicate is from about 10
15 milliequivalents/100 g below the cation exchange capacity of the
untreated silicate to about 30 milliequivalents/100 g above the
cation exchange capacity of the untreated silicate; and

wherein the nanocomposite polyamide material demonstrates,
when tested, an improvement in tensile modulus and flexural
20 modulus, without a substantial decrease in tensile strength, when
compared with that of the polyamide without the layered silicate.

2. The composition of claim 1, wherein the polyamide is
selected from the group consisting of nylon 6, nylon 6,6, nylon

9. The composition of claim 8, wherein the silane coupling agent concentration in the polymer composite is in the range of about 0.5 to 5 weight % of the layered silicate.

10. The composition of claim 1, wherein R_1 is selected from the group consisting of hydrogenated tallow, unsaturated tallow or a hydrocarbon having at least 6 carbons and R_2 , R_3 and R_4 independently have from one to twelve carbons.

11. The composition of claim 1, wherein the ammonium ions are quaternary ammonium ions selected from the group consisting of dimethyldi(hydrogenated tallow) ammonium, dimethylbenzyl hydrogenated tallow ammonium, dimethyl(ethylhexyl) hydrogenated tallow ammonium, trimethyl hydrogenated tallow ammonium, methylbenzyldi(hydrogenated tallow) ammonium, N,N-2-cyclobutoxydi(hydrogenated tallow) ammonium, trimethyl tallow ammonium, methyldihydroxyethyl tallow ammonium and octadecylmethyldihydroxyethyl ammonium, or a mixture thereof.

12. The composition of claim 1, wherein the ammonium ions are quaternary ammonium ions selected from the group consisting of dimethyldi(hydrogenated tallow) ammonium, dimethyl(ethylhexyl) hydrogenated tallow ammonium, dimethylbenzyl hydrogenated tallow ammonium, methyldihydroxyethyl tallow ammonium, or a mixture thereof.

poly(esteramide), poly(etherimide), poly(phenylene sulfide), and poly(phenylene terephthalamide).

19. The composition according to claim 1, wherein said treated silicate particles are treated with a mixture of one or more quaternary ammonium ions with an ammonium ion of the formula



wherein at least one of R_a , R_b and R_c is hydrogen (H) and R_d is selected from a group consisting of a saturated or unsaturated C_1 to C_{22} hydrocarbon, substituted hydrocarbon and branched hydrocarbon, or where R_1 and R_2 form a N,N-cyclic ether.

20. The composition according to claim 19, wherein R_d includes a carboxylic acid moiety.

21. The composition according to claim 19, wherein said mixture includes at least one of dimethyldi(hydrogenated tallow) ammonium, methylhydroxyethyl tallow ammonium and/or dimethyl(ethylhexyl) hydrogenated tallow ammonium in combination with 12-aminolauric acid ammonium.

22. The composition according to claim 1, wherein said layered silicate particles are treated with azine cationic dyes.

23. The composition according to claim 22, wherein the said cationic dyes comprise nigrosines or anthracines.

29. The composition according to claim 1, wherein said composition comprises a composite in which the crystalline regions of the polyamide are less than 1.0 μm .

30. The composition according to claim 1, wherein said
5 composition is in the form of a fiber, film or a molded article.

31. A process to prepare a polyamide nanocomposite composition comprising

(1) forming a flowable mixture of a polyamide and a treated silicate material;

10 (2) dissociating at least about 50% but not all of said treated silicate material to form the nanocomposite composition;

wherein the treated silicate comprises a silicate material treated with at least one ammonium ion of the formula:



15 wherein R_1 , R_2 , R_3 and R_4 are independently selected from a group consisting of a saturated or unsaturated C_1 to C_{22} hydrocarbon, substituted hydrocarbon and branched hydrocarbon, or where R_1 and R_2 form a N,N-cyclic ether; wherein, optionally, one of R_1 , R_2 , R_3 and R_4 is hydrogen;

20 wherein the MER of the treated silicate is from about 10 milliequivalents/100 g below the cation exchange capacity of the untreated silicate to about 30 milliequivalents/100 g above the cation exchange capacity of the untreated silicate; and

37. The process of claim 35, wherein the silane coupling agent concentration in the polymer composite in the range of about 0.5 to 5 weight % of the layered silicate.

38. The process of claim 31, wherein R_1 is selected from the group consisting of hydrogenated tallow, unsaturated tallow or a hydrocarbon having at least 6 carbons and R_2 , R_3 and R_4 independently have from one to twelve carbons.

39. The process of claim 31, wherein the ammonium ion is a quaternary ammonium ion selected from the group consisting of dimethyldi(hydrogenated tallow) ammonium, dimethylbenzyl hydrogenated tallow ammonium, dimethyl(ethylhexyl) hydrogenated tallow ammonium, trimethyl hydrogenated tallow ammonium, methylbenzyldi(hydrogenated tallow) ammonium, methylhydroxyethyl tallow ammonium, and N,N-2-cyclobutoxydi(hydrogenated tallow) ammonium.

40. The process of claim 31, wherein the composition has a concentration of treated layered silicate of from about 0.1 to about 12.0 weight % of the composite.

41. The process of claim 31, wherein the composition has a concentration of treated layered silicate of from about 0.5 to about 6.0 weight % of the composite.

42. The process of claim 31, wherein the treated silicate is dissociated by a method selected from the group consisting of

11, nylon 12, amorphous nylons, aromatic nylons and their copolymers.

50. The process of claim 47, wherein said carrier polymer is of a different weight average molecular weight than
5 said polyamide in said flowable mixture.

51. The process of claim 47, wherein said carrier polymer is a polymer other than a polyamide.

52. The process of claim 47, wherein said carrier polymer has a weight average molecular weight of 10,000 to 40,000 D.

10 53. The process of claim 31, wherein said flowable mixture further comprises a monomer.

54. The process of claim 53, wherein said monomer comprises ϵ -caprolactam, lauryllactam, or their corresponding lactones.

15 55. The process of claim 53, wherein said process further comprises polymerizing said monomer.

56. The process of claim 31, further comprising adding additional amount of said polyamide to said flowable mixture during said dissociating step.

20 57. The process of claim 31 further comprising solid state polymerization or additional melt polymerization of said polyamide.

58. The process of claim 57, wherein the solid state polymerization involves heating the polyamide to a temperature in

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/02768

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08J 5/10; C08K 3/34; C08L 77/00

US CL : 524/445, 448, 449, 442, 789; 523/204, 216

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/445, 448, 449, 442, 789; 523/204, 216

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US A, 5,514,734 (MAXWELL et al.) 07 May 1996, entire document.	1-59
Y	US A, 4,889,885 (USUKI et al.) 26 December 1989, entire document.	1-9,13-20, 22-37,40-59
A	US A, 5,102,948 (DEGUCHI et al.) 07 April 1992	1-59



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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O document referring to an oral disclosure, use, exhibition or other means	
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Date of the actual completion of the international search

22 MAY 1998

Date of mailing of the international search report

19 JUN 1998

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